

“Hydrogen storage in Mg-based alloys”

Thesis

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Introduction

In the last decades it has become obvious, that the polluting and energy consuming life yields the depletion of the natural resources and ecological crisis. The threading global problems e.g. the congestion, the increasing carbon dioxide in the atmosphere and the depletion of ozone layer, need to be solved. The use of polluting fossil energy sources have to change and the alternative energy sources come to the interest. The usage of the alternative energy sources won't solve all the pollution problems but can help in producing an environmental friendly and sustainable energy economy.

The usage of renewable energy sources in the movement of goods and people are impeded by the lack of energy storage and transport solutions. Dissociation of water, by clean energy, is an easy way to produce hydrogen. This hydrogen can be transferred to energy again with very high efficiency (e.g. in fuel cells), thus can be used to power vehicles.

The question of storing hydrogen is one of the main hindering factors. The aim is to store hydrogen in a safe way with the possible highest energy density. It can be stored in tanks under high pressure or at low temperatures, or in absorbed state. Many advanced materials, like carbon nanotubes, metals and intermetallic compounds are capable of storing hydrogen reversibly. In case of same metal-hydrides the achievable energy density is higher than storing the hydrogen is liquid state at 20 K.

To understand the hydrogen absorption and desorption processes is interesting in application and also in scientific point of view. It provides information on the direction of possible future developments. Not only the parameters like maximum capacity and rate have to be monitored, but also their change when exposed to several absorption-desorption processes.

Magnesium-hydride is one of the most attractive and thus widely analyzed hydrogen storage materials because of its high hydrogen storage capacity (~7.6 wt.%), light weight and low environmental impact. However, the wide spread applicability is impeded by its high desorption temperature and sluggish kinetics. To overcome this problem, it is straightforward to refine the microstructure of MgH_2 . Ball milling is a commonly applied technique to reduce the grain size in order to enhance the hydrogen storage properties. Many publications are concerning with these features of MgH_2 in terms of producing conditions and using different catalysts.

Aims

Based on the literature it can be concluded that physicists, chemists and material scientists focus their research on the field of hydrogen storage. This field seems to be strongly interdisciplinary. Our goal was to study the hydrogen storage properties in aspects of materials science.

The aim of this work is to give a short summary of today's most promising storage solutions including metal-hydrides, to study the properties of magnesium hydride in terms of hydrogen storage and to monitor and analyze the microstructural properties during hydrogen absorption-desorption cycles.

We have analyzed the kinetic properties in terms of microstructure and concluded the absorption and desorption processes from the microstructural changes during cycling. We have also examined the effect of adding catalyst on the microstructure and thus on the hydrogen storage properties.

Methods

The hydrogen storage properties (e.g. hydrogen absorption and desorption kinetics and temperature, capacity, activation energy) can be improved by reducing the grain size of magnesium hydride. For this purpose we have used the most widely used technique i.e. ball-milling (BM) to produce pure nanocrystalline MgH_2 and MgH_2 with catalyst.

The morphological properties were characterized by Scanning Electron Microscopy (SEM) and the microstructure by X-ray diffraction (XRD). In order to evaluate the diffractograms, the Convolutional Multiple Whole Profile (CMWP) fitting method developed at ELTE, Department of Materials Physics was applied, which provides more detailed information on the microstructural parameters than conventional XRD evaluation methods. It was shown that the CMWP method is capable to monitor the variation of the microstructural parameters during several desorption-absorption cycles of MgH_2 powders.

The hydrogen absorption-desorption kinetics were analyzed by a Sievert-type apparatus (PCT). The activation energy of desorption was evaluated from thermogravimetric (TG) measurements.

Thesis points

1. Based on the CMWP fitting procedure, it was obtained that the ball-milled MgH_2 powder exhibits a homogeneous microstructure of an average grain size of 9 nm. The first dehydriding-hydriding cycle (activation) results in a coarsened microstructure (20 nm) and a narrow grain-size distribution. Further cycling treatment destroys the homogeneity, while the average grain size remains unchanged. Based on the shrinking core model, the significant difference between the microstructures obtained after the first and repeated cyclings originates from two distinct effects: different average grain size at the beginning of the processes and the different time scale of desorption [1].

2. During a characteristic complete sorption cycle, the initial value of the MgH_2 grain size remains practically unchanged (20 nm) up to 40 % of desorption; however, at the final stage of the $\text{MgH}_2 \rightarrow \text{Mg}$ transformation the remaining small amount of MgH_2 forms very small nanoclusters with an average diameter of 3 nm. This kind of transformation can be ascribed by instantaneous $\text{MgH}_2 \rightarrow \text{Mg}$ conversion of randomly selected particles which is the main characteristics of classical Johnson-Mehl-Avrami (JMA) model. On contrary, a different grain size evolution takes place during the $\text{Mg} \rightarrow \text{MgH}_2$ transformation, i.e. $\langle D \rangle$ increases almost linearly up to 19 nm. The increasing hydride size assumes a Contracting Volume (CV) type of transformation [2].

3. Taking into account the size dependence of a powder agglomerate, the conventional surface controlled (SC), contracting volume and JMA type of sorption functions have been modified by introducing a multi-particle reacted function. For the activation process of nanocrystalline MgH_2 the best fit corresponds to the SC mode, however, the following desorption and absorption processes can be described by the JMA and CV model, respectively. The reaction constants obtained from the multi-particle model can differ from the values of classical single-particle models by 30 percent, indicating that the hydrogen reaction kinetics is strongly affected by the microstructure of nanocrystalline powders [3].

4. We have shown that milling MgH_2 powder in the presence of rigid Nb_2O_5 catalyst particles, the hydride reaches its grain size limit (9-10nm) in a shorter time. The activation energy of the hydrogen desorption is reduced by adding the catalyst, whilst the effect of grain size is negligible. On contrary, the desorption temperature is strongly affected by the average

grain size, which can further be decreased slightly by the presence of the catalyst (altogether by 70 °C compared to the polycrystalline state) [4-6].

5. Based on PCT measurements, we have concluded that the absorption rate is mainly affected by the microstructure, the direct effect of the catalyst is small. In the nanosized regime, the required diffusion length of the hydrogen atoms is drastically reduced, resulting in an enhanced H-uptake [6,7].

Publications

1. D. Fátay, T. Spassov, P. Delchev, G. Ribárik, Á. Révész
„Microstructural development in nanocrystalline MgH_2 during H-absorption/desorption cycling”
International Journal of Hydrogen Energy 32(14): 2914-2919, 2007
I.F.:3,45 Number of independent citations: 5
2. Á. Révész, D. Fátay
„Microstructural evolution of ball-milled MgH_2 during a complete dehydrogenation-hydrogenation cycle”
Journal of Power Sources, *Submitted*
3. Á. Révész, D. Fátay, T. Spassov
„Hydriding kinetics of ball-milled nanocrystalline MgH_2 powders”
Journal of Materials Research 22 (11): 3144-315, 2007
I.F.:1,74 Number of independent citations: 0
4. Á. Révész, D. Fátay, T. Spassov
„Microstructure and hydrogen desorption of nanocrystalline MgH_2 with 5 mole% V_2O_5 and Nb_2O_5 as catalyst”
Absztrakt, 7th Int. Conference on Nanostructured Materials, 20-24 June, 2004, Wiesbaden, Germany
5. D. Fátay, Á. Révész, T. Spassov
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Journal of Alloys and Compounds 399 (1-2): 237-241, 2005
I.F.:1,51 Number of independent citations: 24

6. Á. Révész, D. Fátay, T. Spassov

„Microstructure and hydrogen sorption kinetics of Mg nanopowders with catalyst”

Journal of Alloys and Compounds 434: 725-728, 2007

I.F.:1,51

Number of independent citations: 5

7. Á. Révész, D. Fátay, D. Zander, T. Spassov

„Influence of particle size on the hydrogen sorption properties of ball-milled MgH_2 with Nb_2O_5 as catalyst”

Journal of Metastable and Nanocrystalline Materials, 24-25: 447-450, 2005

I.F.: -

Number of independent citations: 1